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FINAL REPORT

on

HAZARD ANALYSIS OF ONTARIO WASTE MANAGEMENT INDUSTRIAL WASTE TREATMENT AND DISPOSAL FACILITY

Phase II - Probability Analysis of Tank Farm Fire Involving Vaporization of Halogen-Organic Waste

to

ONTARIO WASTE MANAGEMENT CORPORATION

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by

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EXECUTIVE SUMMARY

The Ontario Waste Management Corporation contracted with Battelle's Columbus Laboratories to do a Hazard Analysis of their Industrial Waste Treatment and Disposal Facility. Phase II - Probability Analysis of Tank Farm Fire Involving Vaporization of Halogen-Organic Waste is reported here.

An accident has been hypothesized which involves a leak in a halogen-organic waste tank. It is assumed that the waste collects within the diked area around the tank, is somehow ignited and may volatilize enough of the halogen-organic constituent remaining in the tank, through a vent 10 meters above ground level, to produce an unacceptable concentration at the facility boundary. The probability that such a fire might occur becomes an important factor in determining the risk that this type of accident represents. An analysis to determine the probability was conducted.

An event tree/fault tree analysis was made to delineate the accident event sequences of interest and the faults that might contribute to this accident. From this analysis it was found that the probability of a leak or spill in the diked area from failure of containment, failure of other equipment and/or human error is 2.6×10^{-2} per year or one chance in 38 per year.

Data from oil refinery operations suggest that ignition probability, given a spill, is 1/20 to 1/33. If this factor is representative of the halogen-organic storage tank area, the probability of volatilizing the halogen-organic is about once in 770 to 1300 years.

The effects of mitigative measures such as:

1. Detecting the spill before ignition,
2. Preventing immediate/delayed ignition or
3. Suppressing fire before vaporization is significant

have not been considered. If necessary, the value of detection, draining the tank before ignition, fire fighting, etc. can be conservatively estimated by those familiar with those operations to arrive at a more

realistic probability of the accident going to completion. Before doing that however, the consequence analysis should be reviewed to determine the probability that a person might be at the facility boundry at the time of the accident.

An alternative scenario considers the possibility of a fire in the adjacent diked area caused by a leak in an organic sludge tank in that area. The question is whether the fire will radiate enough heat to the adjacent halogen-organic tanks to cause the same hazard at the facility boundary. A first order analysis of this radiative heat transfer problem was made to see if this scenario might cause a serious problem.

The organic sludge tank volume is 120 cubic meters. If one tank is emptied into the dike area it will fill it to a depth of 0.23 meters. If we assume the contents are a hydrocarbonlike combustible it will burn at a rate of about 5 mm/min. This yields a burning time of 46 minutes for one tank of organic sludge.

With a few approximations an effective area of 3.83 square meters (41.2 square feet) can be determined for the tank exposed to the essentially half-infinite flame a distance of 2.6 meters from the tank centerline. If, as is likely, the organic sludges will burn with a sooty flame we can assume a black body flame surface at 1600F. Such a flame emits 31,150 Btu/hr-square ft. Thus the tank will be absorbing about 1,283,400 Btu/hr. Reradiation can be neglected because the internal boiling will hold the tank wall temperature to a low level.

From the physical properties of the halogen-organic (methylene chloride is considered for this example) we can calculate that it will take 352 kJ/kg (151 Btu/lb) to heat the liquid to its boiling temperature from an ambient of 21C (70F) and vaporize it at atmospheric pressure. At 10 psig, the pressure at which the vent control valve is set, it will take about twice as much heat to raise its temperature to the boiling temperature but somewhat less to vaporize it and the effects of pressure act to partially cancel each other. (The latent heat of vaporization at 10 psig is not available but it is less than at one atmosphere). If the waste were 100% methylene chloride, 9,040 kg (19,900 lb), it would take about 9 minutes to raise its temperature to the boiling point at atmospheric pressure and about 15 minutes at 10 psig. From that point on about 69 kg (151 lb) of methylene

chloride would be vaporized each minute at atmospheric pressure and somewhat more than that at 10 psig. During the remaining 37 or 31 minutes of the fire, depending upon the time to reach boiling temperature, up to 2,550 kg (5,600 lb) of methylene chloride might be vaporized from one tank. This is about 28% of the tank volume.

A preliminary calculation was made to estimate the value of insulating the halogen-organic tanks. The time to reach vaporization temperature can be increased to several hours, until long after the fire has burned itself out, by 3 or 4 inches of insulation. However, the insulation would have to withstand temperatures substantially above 540C (1000F).

The probability of a sludge tank failure, and hence the probability of this second scenario, can reasonably be estimated to be the same as that for a halogen-organic waste tank; that is, 2.6×10^{-2} per year.

Finally, if it is assumed that all sludge tanks and halogen-organic tanks are in full usage (9 tanks) then the probability of a leak and a fire with volatilization of the halogen-organic can be estimated to be between one chance in four per year, if ignition is assumed to occur with a probability of one, or one chance in 100 per year if ignition occurs once per 25 spills. However, addition of insulation to the halogen-organic tank, as well as other mitigative measures, appear to offer effective mitigation for tank farm fires such as hypothesized.

The possibility of phosgene production during methylene chloride/solvent combustion arose during the course of this work. A brief study showed that phosgene might be produced and that either benzene or toluene vapors from the waste may ameliorate this condition. Application of water fogs may lessen the release by destruction of the toxic agent.

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HAZARD ANALYSIS OF ONTARIO WASTE MANAGEMENT INDUSTRIAL WASTE TREATMENT AND DISPOSAL FACILITY

Phase II - Probability Analysis of Tank Farm Fire Involving Vaporization of Halogen-Organic Waste

INTRODUCTION

Battelle Columbus Division has been assisting the Ontario Waste Management Corporation in the development of a hazardous waste treatment and disposal facility for the Province of Ontario by conducting a hazard analysis.

One of the hazards that has been hypothesized in earlier work is the possibility of a fire in the organic waste storage farm area that heats a tank containing a halogen-organic waste such as methylene chloride. It has been estimated that if the fire were within the dike of the halogen-organic waste tank such that the fire surrounded the tank, it might volatilize sufficient halogen-organic to produce an unacceptable concentration at the boundary of the facility. Battelle was asked to calculate the probability of such a fire and release of halogen-organic vapor to the atmosphere.

A second scenario which could result in the release of halogen-organic vapor involves a fire within the adjacent diked area which has six organic sludge tanks. In this case the fire would not surround the halogen-organic waste tanks but the heat radiated from the fire might be sufficient to cause a release of vapor from the halogen-organic tanks. At the kick-off meeting on Phase II at the MONENCO offices in St. Catharines this second scenario was discussed and Battelle was asked to do a first order analysis to see if the heat radiated from such a fire could lead to an unacceptable release of methylene chloride vapor. In subsequent telephone conversations, it was pointed out that an analysis of the probability of the second scenario would be needed if the consequences might be unacceptable.

During the course of this investigation, a question arose concerning the combustion of methylene chloride. Although not flammable in air at normal temperatures, methylene chloride is combustible at the high temperatures of the burning solvent and phosgene may be a combustion product. This was studied briefly and the results are included as Appendix A in this report.

ANALYSIS OF THE PROBABILITY OF A FIRE WITHIN THE DIKES OF THE HALOGEN-ORGANIC WASTE AREA THAT COULD CAUSE UNACCEPTABLE VENTING OF HALOGEN-ORGANIC VAPOR TO THE ATMOSPHERE

Introduction

Figure 1 (Figures and Tables are at the end of this section.) shows the event tree for the tank farm fire problem that was analyzed. Table 1 defines the specific outcomes on the event tree. The event tree reflects the expected path of the accident allowing for the possibility of either immediate ignition or delayed ignition if the spill remains undetected. The fault tree presented in Figure 2 specifically addresses the spill of flammable material (containing a halogen-organic) around the storage tank (Event S in the event tree).

The fault tree for Event S, spill of flammable material around the tank, considers spills from the following three types of events.

1. Leak/rupture failure of tank, piping, or equipment.
2. Underpressure failure of the halogenated waste storage tank.
3. Spills from storage tank after tank flushing due to errors in the flush procedure. This event considers only those maintenance-related spills that might occur after the maintenance personnel have left the dike area.

These three types of events address the important spills that might fuel a fire within the storage tank dike. Overpressure failure of the halogen-organic waste storage tank is not specifically considered in Event S. The accident sequence assumes successful pressure relief from the tank (Event R in the event tree).

Events I, C, D, F, and R of the event tree do not require fault tree models. Events I and D, the ignition events, require only identification of potential ignition sources and an estimate of the ignition probability. Events C and F are assumed failed in the quantification. Event R

of the event tree is assumed successful in the quantification to conform with the accident as hypothesized.

It is also important to note what is not considered in the analysis. The analysis does not examine the effects of the following events:

- Loss of electric power,
- Loss of plant air,
- Loss of firewater system, and
- Loss of nitrogen.

These events may become important as the specifications for the valve actuators, instrumentation, and control systems mature. Rather than attempt a premature evaluation of these events at this time, we expect that insights gained from the current task can be beneficial in formulating these specifications. Also, external events are not specifically included in the models.

Modeling Assumptions

The fault tree models are based on the following assumptions after discussions with Monenco personnel.

1. Figures 3 and 4 show the equipment and instrumentation of the halogenated waste storage tank as they are modeled in the fault tree, and the tank system.

2. The pump used to fill the halogenated storage tanks is designed to stop on high pressure resulting from closure of the storage tank inlet valve if the operator fails to stop the pump based on tank level indication.

3. The capacity of a truck being unloaded is assumed to be larger than the storage tank capacity.

4. The interlock logic associated with the storage tank inlet valve provides a warning to the operator when the tank is full. The operator is required to check the data management system prior to aligning a particular unloading bay to a storage tank.

5. Vacuum relief is provided for each group of storage tanks. The vacuum relief valve is located on the vent header between the two pressure control valves.

6. One vent line from the storage tanks to the overflow tank handles both liquid and vapor flow.

7. The overflow tank has both pressure and vacuum relief valves.

8. The carbon adsorbers do not mitigate the toxic effects of a release resulting from a fire around the storage tank.

9. The incinerator is not capable of handling the vapor flow resulting from a fire around the storage tank. Therefore, the incinerator is not considered as a possible relief path.

10. The quantitative analysis assumes that each of the three halogenated storage tanks is filled and emptied approximately 60 times per year.

11. A procedure for the yearly flushing of the storage tanks was assumed to allow inclusion of operator errors that might contribute to spills within the dike. The assumed procedure is included as Table 2.

Leak Size Within the Dike

A leak of flammable material within the dike must be large enough to sustain a fire for a period of time long enough to bring the contents of the tank to boiling. Estimates of leak sizes were made to determine if any potential failure modes could be eliminated from the fault tree model or segregated in the subsequent quantification. These estimates were based on the following assumptions.

1. The area contained within a dike of a single halogenated storage tank is approximately 58.8 m^2.

2. A pool of material within the dike would burn at the rate of 5 mm/minute.

3. Four minutes of a fully developed fire surrounding the tank results in boiling of the tanks contents; therefore, the critical spill size within the dike is approximately 14.8% of a full tank, or 1.18 m^3.

4. Operators inspect the dike once per dayshift (once every 24 hours). Assuming a spill would be detected on the next inspection, the minimum leak rate that would result in a spill larger than 1.18 m^3 in 24 hours is 0.0008 m^3/minute.

5. Assuming a leak from the bottom of the tank, this leak rate corresponds to a hole in the tank with a diameter of approximately 1.5 mm.

This relatively small leak size does not permit the removal of any potential failure modes identified in the fault tree. Also, available data for leak rates are not sufficiently detailed to allow segregation of the probabilities for leak and rupture based on this leak size. The quantification of the fault tree therefore considers a single probability for the postulated leak/rupture events.

Results

The results of the fault tree analysis consist of two parts; (1) the minimal cut sets from the fault tree, and (2) a quantitative estimate of the frequency of spills within the dike. The minimal cut sets are the minimal combinations of equipment failure and/or human error that can result in a spill within the dike. Table 3 contains the listing of the minimal cut sets from the fault tree. The frequency estimate is based on failure data for each of the failure events identified in the fault tree. Table 4 contains the probability estimates for each of the fault tree events.

The results of the analysis estimate the frequency of the spill within the dike as 2.6×10^{-2} per year, or about once in 38 years for an individual halogenated storage tank. About 53% of the total frequency is the result of the leak/rupture events associated with piping, connections, and the storage tank. Forty-six percent of the total frequency is associated with spills resulting from errors in the tank flushing procedure. In fact, one failure in this category -- failure to close and verify the discharge flush valve after tank flushing -- contributes 38% of the total frequency. If this event occurs, waste material will spill through the flush valve when the tank discharge valve is opened to permit the waste to be pumped from the tank.

There are few potential ignition sources within the dike of the tank farm. The tank agitator and the instrumentation provide sources of electrical energy that might potentially ignite a spill and, therefore, Class 1 protected equipment is specified. Ignition will depend chiefly on the waste material that is spilled and whether vapor from the spill will approach an ignition source in a flammable mixture. Based on the limited number of potential ignition sources and available data, the ignition probability is estimated to be 0.03 to 0.05 per spill (one in 33 to one in 20).

In summary, taking no credit for spill detection and cleanup or fire-fighting efforts, and assuming that the storage tank does not fail from overpressure, the frequency of spills followed by fires that might result in an unacceptable release of halogen-organic vapor is estimated as 7.8×10^{-4} to 1.3×10^{-3} per year, or once in 770 to 1,300 years.

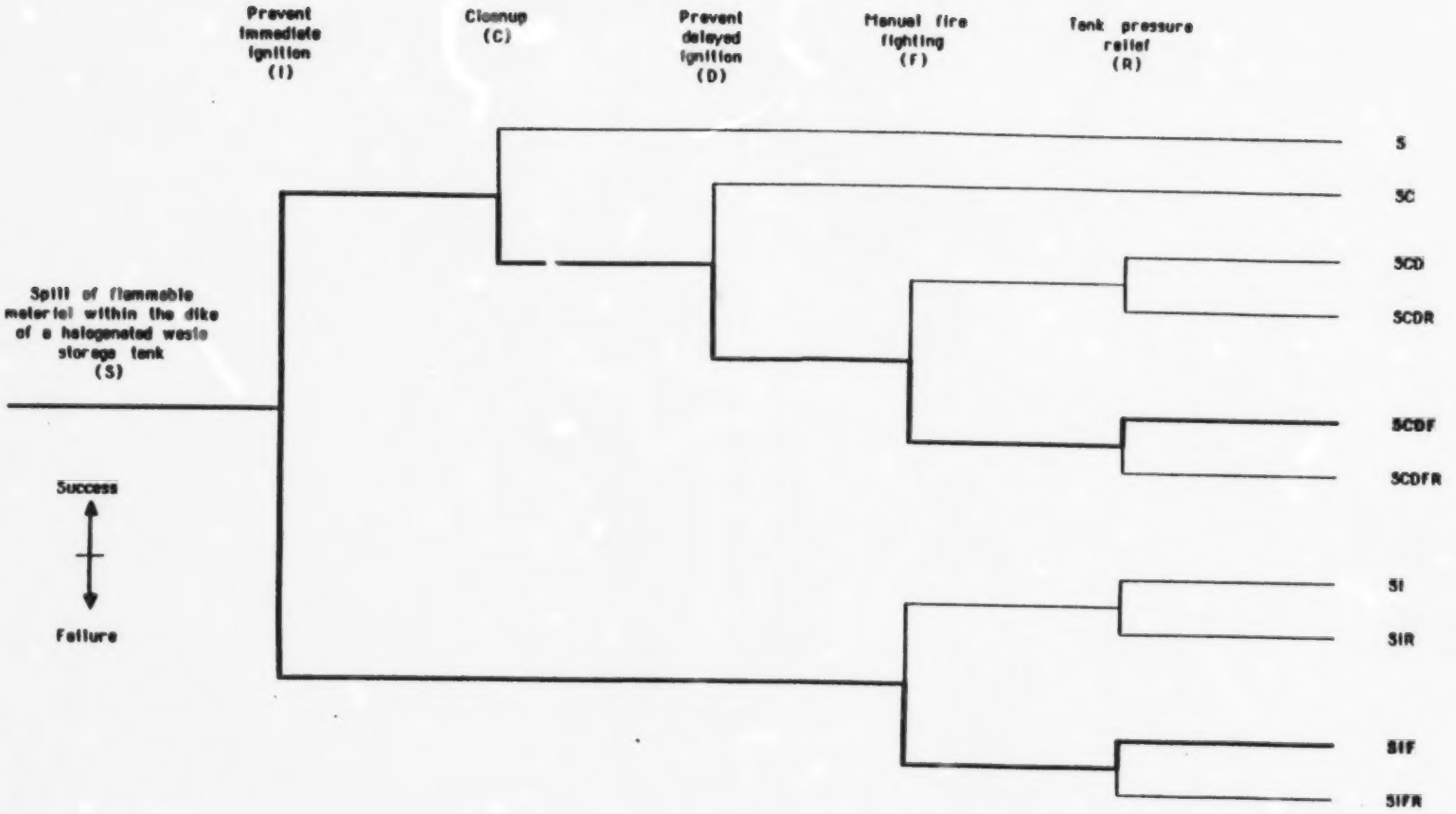

FIGURE 1. EVENT TREE FOR TANK FARM FIRE

TABLE 1. EVENT SEQUENCE OUTCOMES

S - Spill. No fire, no release except vapors from spill.

SC - Spill with no cleanup. No fire, no release except vapors from spill.

SCD - Spill, no cleanup, delayed ignition. Release via fire and vent (short-term).

SCDR - Spill, no cleanup, delayed ignition, relief failure. Release via fire, pressure buildup in tank (short-term).

SCDF - Spill, no cleanup, delayed ignition, no fire fighting. Release via fire and vent (long-term).

SCDFR - Spill, no cleanup, delayed ignition, no fire fighting, relief failure. Release via fire, pressure buildup in tank (long-term).

SI - Spill, immediate ignition. Release via fire and vent (short-term).

SIR - Spill, immediate ignition, relief failure. Release via fire, pressure buildup in tank (short-term).

SIF - Spill, immediate ignition, no fire fighting. Release via fire and vent (long-term).

SIFR - Spill, immediate ignition, no fire fighting, relief failure. Release via fire, pressure buildup in tank (long-term).

Notes: 1. "Short term" indicates that manual fire fighting was successful in mitigating release.

2. "Long term" indicates no mitigation by fire fighting

3. The event sequences in bold type, SDCF and SIF, are the hypothesized scenarios that were analyzed.

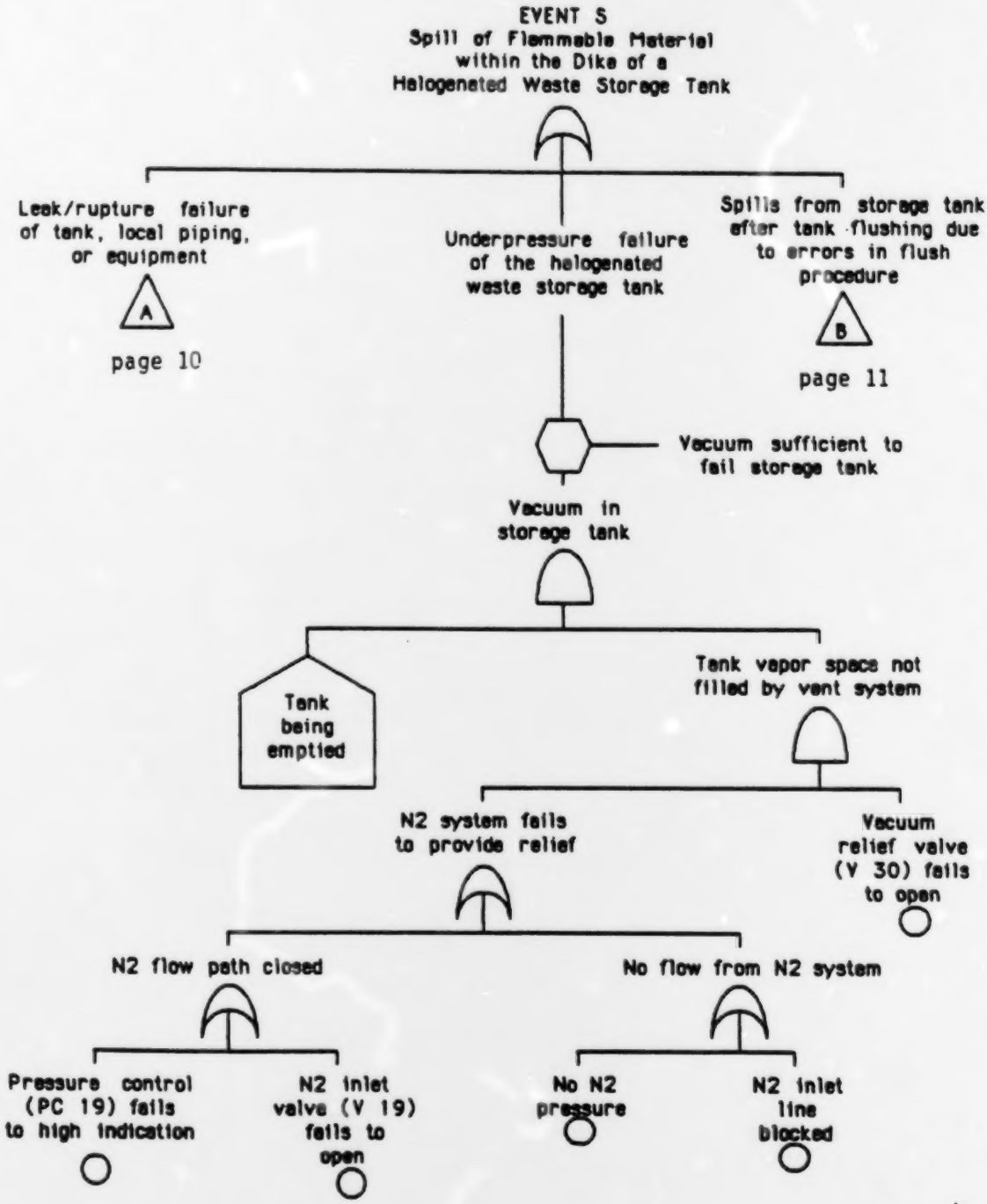
EVENT S
Spill of Flammable Material within the Dike of a Halogenated Waste Storage Tank
Leak/rupture failure of tank, local piping, or equipment
A
page 10
Underpressure failure of the halogenated waste storage tank
Spills from storage tank after tank flushing due to errors in flush procedure
B
page 11
Vacuum sufficient to fail storage tank
Vacuum in storage tank
Tank being emptied
Tank vapor space not filled by vent system
N2 system fails to provide relief
Vacuum relief valve (V 30) fails to open
N2 flow path closed
No flow from N2 system
Pressure control (PC 19) fails to high indication
N2 inlet valve (V 19) fails to open
No N2 pressure
N2 inlet line blocked

FIGURE 2. FAULT TREE MODEL FOR EVENT S

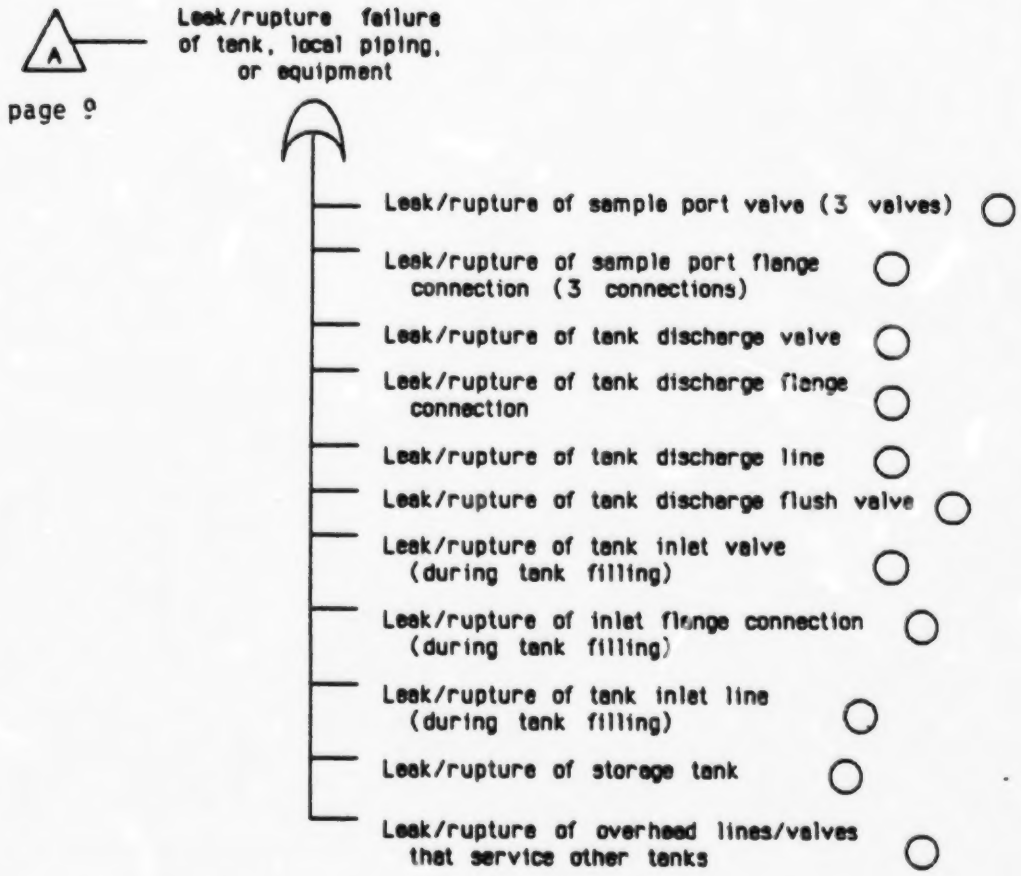
A
Leak/rupture failure of tank, local piping, or equipment
page 9
Leak/rupture of sample port valve (3 valves)
Leak/rupture of sample port flange connection (3 connections)
Leak/rupture of tank discharge valve
Leak/rupture of tank discharge flange connection
Leak/rupture of tank discharge line
Leak/rupture of tank discharge flush valve
Leak/rupture of tank inlet valve (during tank filling)
Leak/rupture of inlet flange connection (during tank filling)
Leak/rupture of tank inlet line (during tank filling)
Leak/rupture of storage tank
Leak/rupture of overhead lines/valves that service other tanks

FIGURE 2. FAULT TREE MODEL FOR EVENT S (Continued)

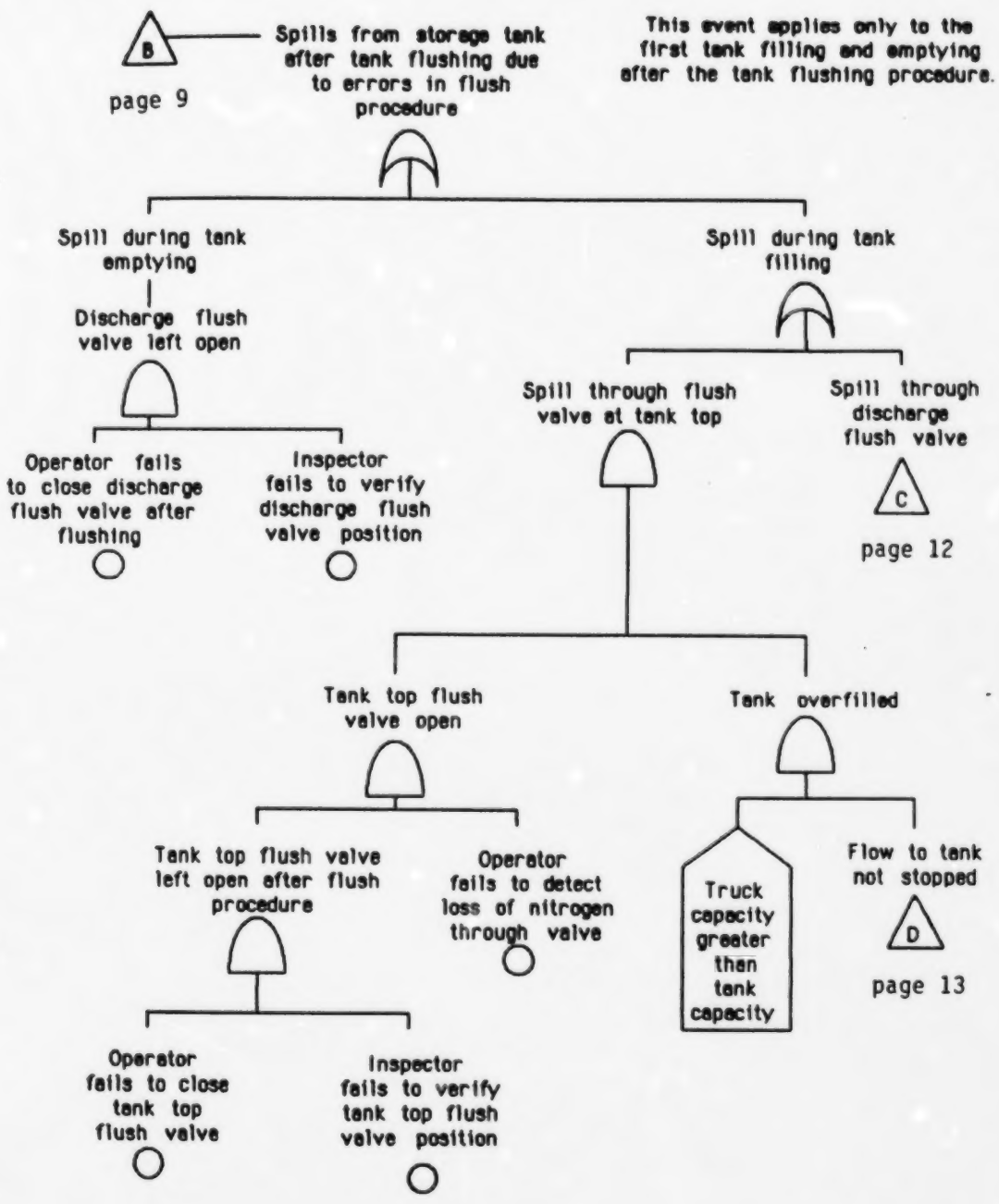
B
page 9
Spills from storage tank after tank flushing due to errors in flush procedure
This event applies only to the first tank filling and emptying after the tank flushing procedure.
Spill during tank emptying
Discharge flush valve left open
Operator fails to close discharge flush valve after flushing
Inspector fails to verify discharge flush valve position
Spill during tank filling
Spill through flush valve at tank top
Spill through discharge flush valve
C
page 12
Tank top flush valve open
Tank top flush valve left open after flush procedure
Operator fails to close tank top flush valve
Inspector fails to verify tank top flush valve position
Operator fails to detect loss of nitrogen through valve
Tank overfilled
Truck capacity greater than tank capacity
Flow to tank not stopped
D
page 13

FIGURE 2. FAULT TREE MODEL FOR EVENT S (Continued)

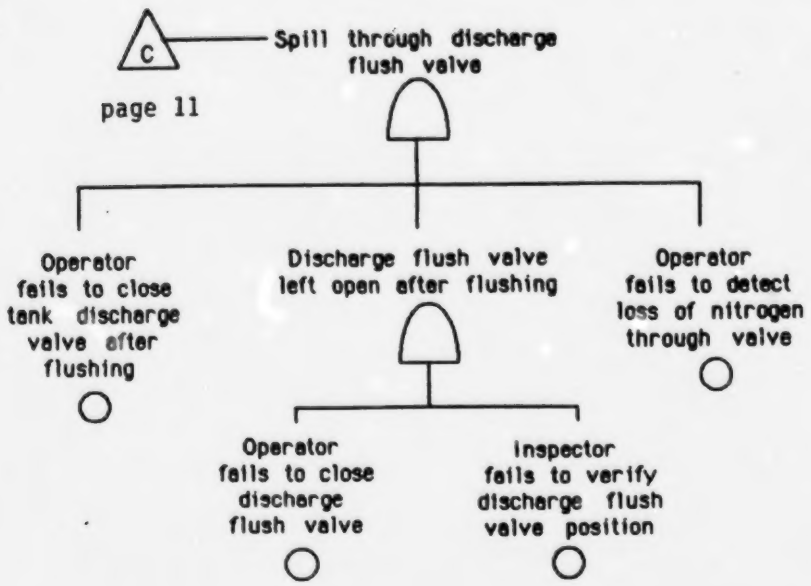
C
Spill through discharge flush valve
page 11
Operator fails to close tank discharge valve after flushing
Discharge flush valve left open after flushing
Operator fails to detect loss of nitrogen through valve
Operator fails to close discharge flush valve
Inspector fails to verify discharge flush valve position

FIGURE 2. FAULT TREE MODEL FOR EVENT S (Continued)

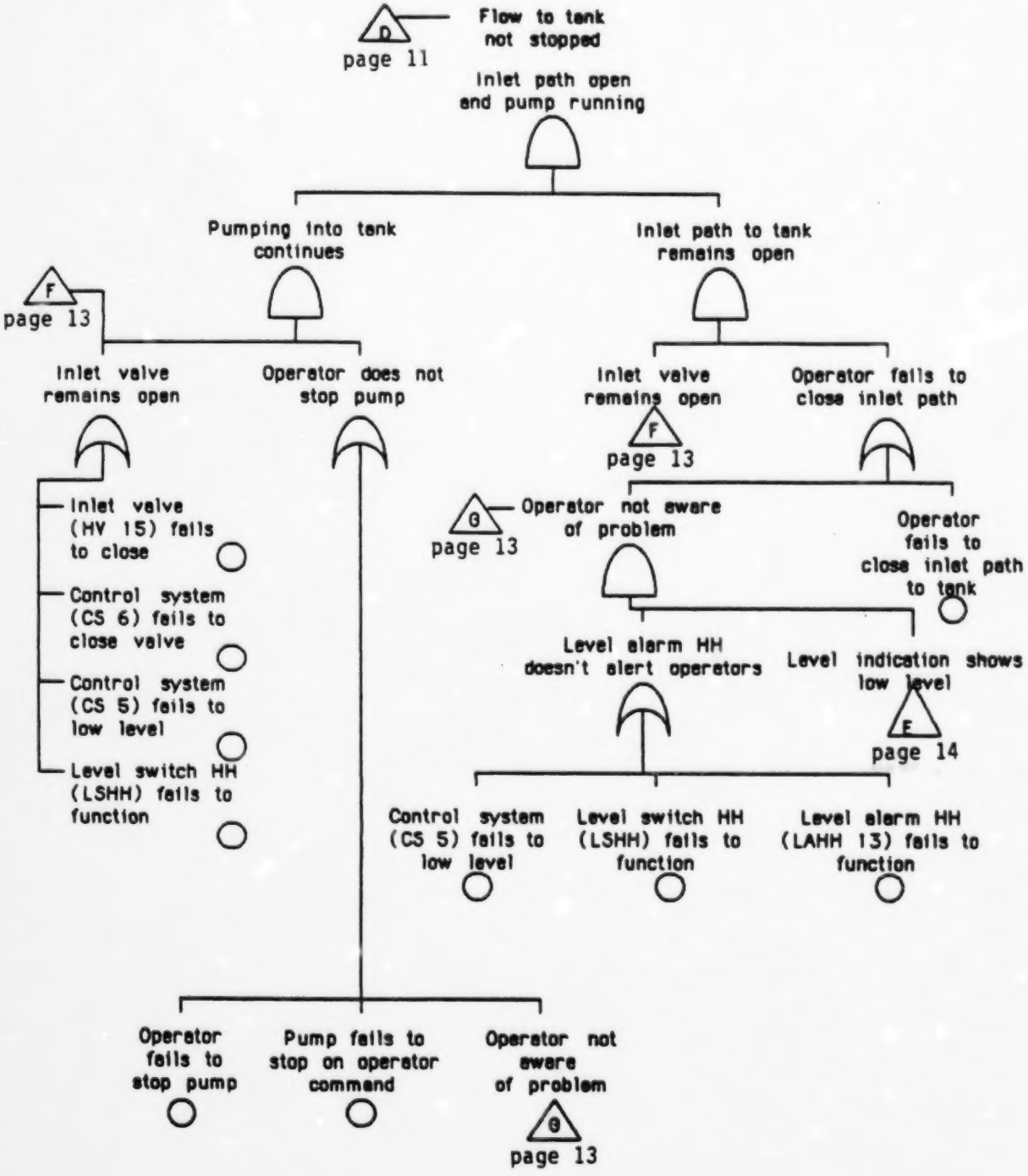
D
page 11
Flow to tank not stopped
Inlet path open and pump running
Pumping into tank continues
Inlet path to tank remains open
F
page 13
Inlet valve remains open
Operator does not stop pump
Inlet valve remains open
Operator fails to close inlet path
F
page 13
Inlet valve (HV 15) fails to close
Control system (CS 6) fails to close valve
Control system (CS 5) fails to low level
Level switch HH (LSHH) fails to function
G
page 13
Operator not aware of problem
Operator fails to close inlet path to tank
Level alarm HH doesn't alert operators
Level indication shows low level
E
page 14
Control system (CS 5) fails to low level
Level switch HH (LSHH) fails to function
Level alarm HH (LAHH 13) fails to function
Operator fails to stop pump
Pump fails to stop on operator command
Operator not aware of problem
G
page 13

FIGURE 2. FAULT TREE MODEL FOR EVENT S (Continued)

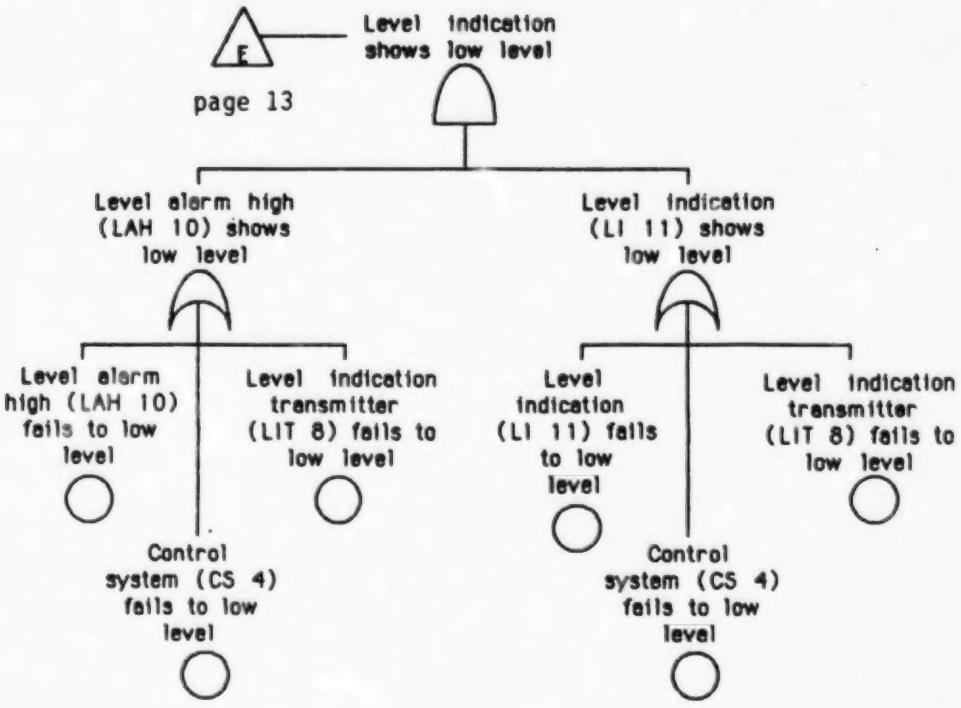
E
Level indication shows low level
page 13
Level alarm high (LAH 10) shows low level
Level indication (LI 11) shows low level
Level alarm high (LAH 10) fails to low level
Level indication transmitter (LIT 8) fails to low level
Control system (CS 4) fails to low level
Level indication (LI 11) fails to low level
Level indication transmitter (LIT 8) fails to low level
Control system (CS 4) fails to low level

FIGURE 2. FAULT TREE MODEL FOR EVENT S (Continued)

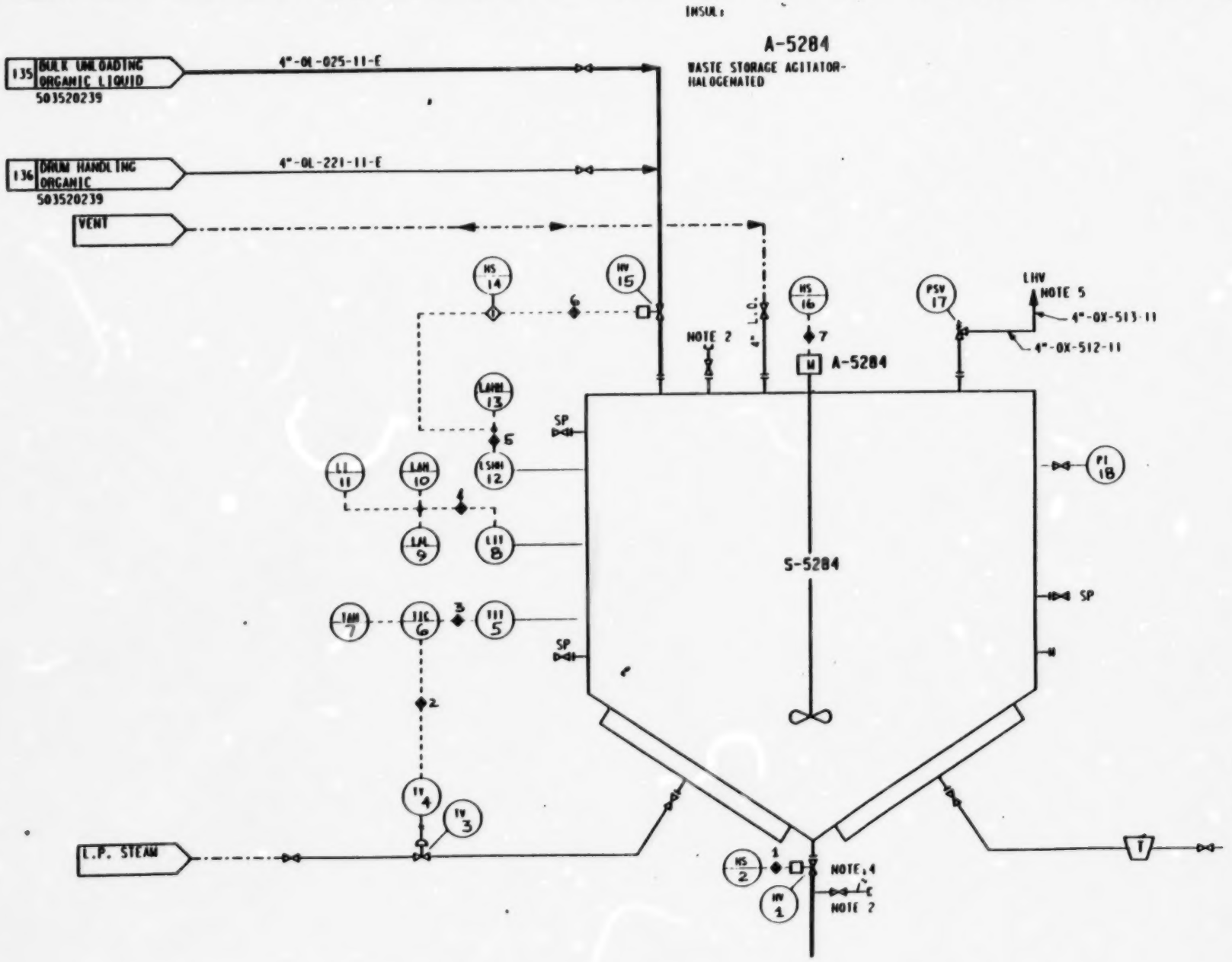

FIGURE 3. HALOGENATED WASTE STORAGE TANK CONFIGURATION

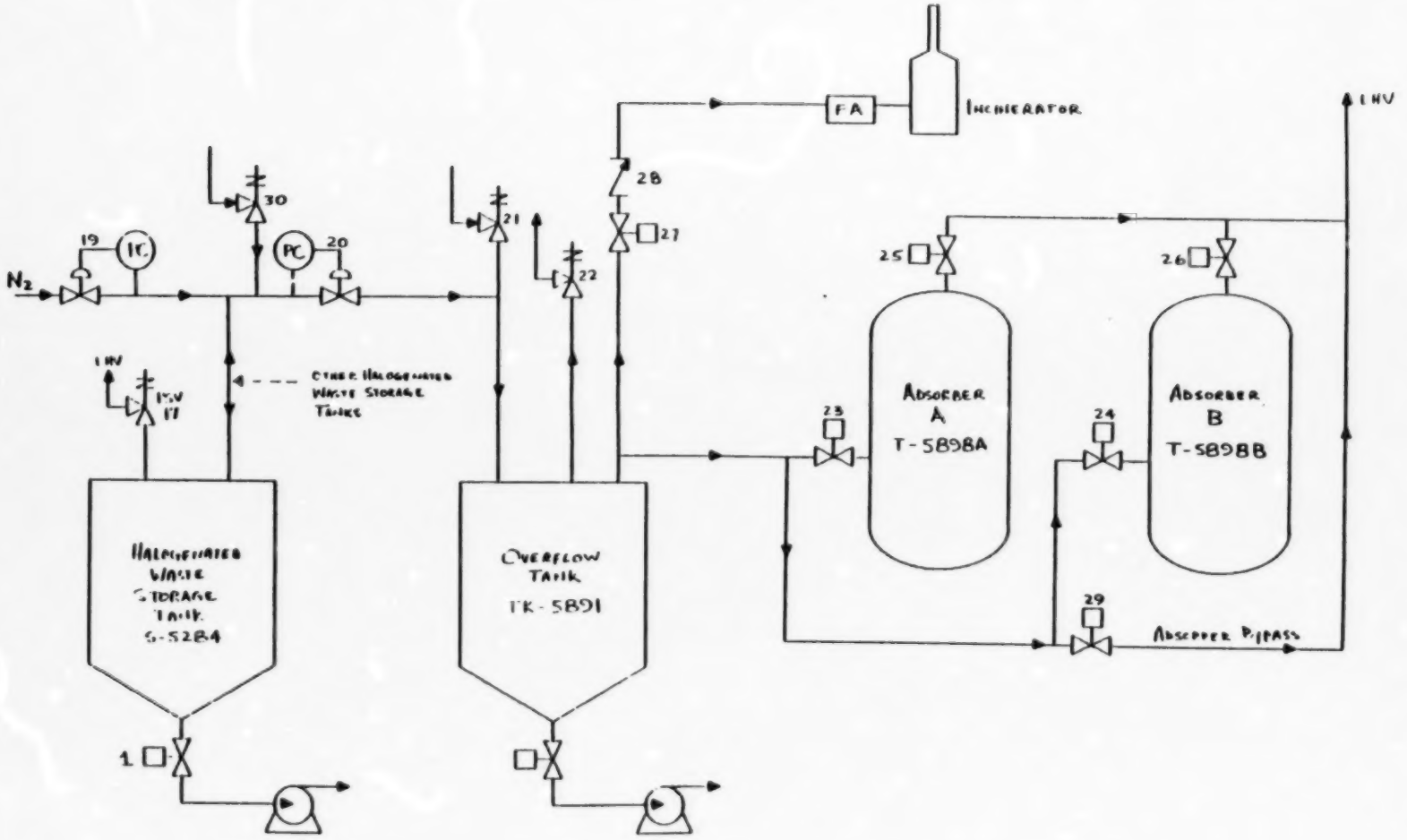

FIGURE 4. SYSTEM AS ASSUMED FOR FAULT TREE MODELING

TABLE 2. ASSUMED PROCEDURE FOR TANK FLUSHING OPERATION

The yearly flushing of the storage tanks offers an opportunity for spill of the material due to procedural errors in returning the tank to service. Since the actual procedure has not been established, we have assumed the following tank flushing procedure in developing the models.

1. Drain and isolate tank
    - 1.1 Open tank discharge valve
    - 1.2 Pump out tank contents
    - 1.3 Close pump suction valve in discharge line
    - 1.4 Close and lock out tank inlet valve
2. Connect hoses to flush connections
    - 2.1 Remove blind from discharge flush connection
    - 2.2 Connect hose to discharge flush connection
    - 2.3 Remove blind from tank top flush connection
    - 2.4 Connect hose to flush connection on tank top
3. Flush tank
    - 3.1 Open flush valve on tank top
    - 3.2 Turn on flush water, fill tank
    - 3.3 Turn off flush water
    - 3.4 Open discharge flush valve, drain tank
4. Disconnect hoses from tank
    - 4.1 Close flush valve on tank top
    - 4.2 Disconnect hose from valve on tank top
    - 4.3 Reinstall blind on tank top flush valve
    - 4.4 Close discharge flush valve
    - 4.5 Disconnect hose from discharge flush valve
    - 4.6 Reinstall blind on discharge flush valve
5. Return tank to service
    - 5.1 Verify closure of flush valve on tank top
    - 5.2 Verify closure of discharge flush valve
    - 5.3 Close tank discharge valve
    - 5.4 Open pump suction valve in tank discharge line
    - 5.5 Unlock/return tank inlet valve to service

TABLE 3. MINIMAL CUTSETS FOR EVENT S

EVENT S
HALOGENATED STORAGE TANK UNDERPRESSURE FAILURE
(Assume vacuum is sufficient to fail the storage tank)

1. Tank being emptied,
   Vacuum relief valve (V 30) fails to open,
   pressure control (PC 19) fails to high indication.

2. Tank being emptied,
   Vacuum relief valve (V 30) fails to open,
   N2 inlet valve (V 19) fails to open.

3. Tank being emptied,
   Vacuum relief valve (V 30) fails to open,
   no N2 pressure.

4. Tank being emptied,
   Vacuum relief valve (V 30) fails to open,
   N2 inlet line blocked.

TABLE 3. MINIMAL CUTSETS FOR EVENT S (Continued)

LEAK/RUPTURE OF LOCAL PIPING OR EQUIPMENT

1. Leak/rupture of sample port valve (3 valves).
2. Leak/rupture of sample port flange connection (3 connections).
3. Leak/rupture of tank discharge valve.
4. Leak/rupture of tank discharge flange connection.
5. Leak/rupture of tank discharge line.
6. Leak/rupture of tank discharge flush valve.
7. Leak/rupture of tank inlet valve (during tank filling).
8. Leak/rupture of inlet flange connection (during tank filling).
9. Leak/rupture of tank inlet line (during tank filling).
10. Leak/rupture of storage tank.
11. Leak/rupture of overhead lines/valves that service other tanks.

TABLE 3. MINIMAL CUTSETS FOR EVENT S (Continued)

SPILL FROM STORAGE TANK AFTER TANK FLUSHING DUE TO ERROR IN FLUSH PROCEDURE

(This event applies only to the first filling and emptying of the tank after the flush procedure, approximately once per year).

A. Spill during tank emptying.

1. Operator fails to close discharge flush valve after flushing,
   inspector fails to verify discharge flush valve position.

B. Spill during tank filling.

2. Operator fails to close discharge flush valve,
   inspector fails to verify dsicharge flush valve position,
   operator fails to detect nitrogen loss through valve,
   operator fails to close tank discharge valve after flushing.

3. Truck capacity greater than tank capacity,
   operator fails to close tank top flush valve,
   inspector fails to verify tank top flush valve position,
   operator fails to detect loss of nitrogen through valve,
   control system (CS 5) fails to low level,
   control system (CS 4) fails to low level.

4. Truck capacity greater than tank capacity,
   operator fails to close tank top flush valve,
   inspector fails to verify tank top flush valve position,
   operator fails to detect loss of nitrogen through valve,
   control system (CS 5) fails to low level,
   level indication transmitter (LIT 8) fails to low level.

5. Truck capacity greater than tank capacity,
   operator fails to close tank top flush valve,
   inspector fails to verify tank top flush valve position,
   operator fails to detect loss of nitrogen through valve,
   level switch HH (LSHH) fails to function,
   control system (CS 4) fails to low level.

TABLE 3. MINIMAL CUTSETS FOR EVENT S (Continued)

6. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
level switch HH (LSHH) fails to function,
level indication transmitter (LIT 8) fails to low level.

7. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
operator fails to stop pump,
operator fails to close inlet path to tank,
control system (CS 5) fails to low level.

8. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
pump fails to stop on operator command,
operator fails to close inlet path to tank,
control system (CS 5) fails to low level.

9. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
operator fails to stop pump,
operator fails to close inlet path to tank,
level switch HH (LSHH) fails to function.

TABLE 3. MINIMAL CUTSETS FOR EVENT S (Continued)

10. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
operator fails to stop pump,
operator fails to close inlet path to tank,
control system (CS 6) fails to close valve.

11. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
operator fails to stop pump,
operator fails to close inlet path to tank,
inlet valve (HV 15) fails to close.

12. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
pump fails to stop on operator command,
operator fails to close inlet path to tank,
level switch HH (LSHH) fails to function.

13. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
pump fails to stop on operator command,
operator fails to close inlet path to tank,
control system (CS 6) fails to close valve.

TABLE 3. MINIMAL CUTSETS FOR EVENT S (Continued)

14. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
pump fails to stop on operator commend,
operator fails to close inlet path to tank,
inlet valve (HV 15) fails to close.

15. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
level alarm HH (LAHH 13) fails to function,
control system (CS 6) fails to close valve,
control system (CS 4) fails to low level.

16. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
level alarm HH (LAHH 13) fails to function,
inlet valve (HV 15) fails to close,
control system (CS 4) fails to low level.

17. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
level alarm HH (LAHH 13) fails to function,
control system (CS 6) fails to close valve,
level indication transmitter (LIT 8) fails to low level.

TABLE 3. MINIMAL CUTSETS FOR EVENT S (Continued)

18. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
level alarm HH (LAHH 13) fails to function,
inlet valve (HV 15) fails to close,
level indication transmitter (LIT 8) fails to low level.

19. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
control system (CS 5) fails to low level,
level alarm high (LAH 10) fails to low level,
level indication (LI 11) fails to low level.

20. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
level switch HH (LSHH) fails to function,
level alarm high (LAH 10) fails to low level,
level indication (LI 11) fails to low level.

21. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
level alarm HH (LAHH 13) fails to function,
control system (CS 6) fails to close valve,
level alarm high (LAH 10) fails to low level,
level indication (LI 11) fails to low level.

TABLE 3. MINIMAL CUTSETS FOR EVENT S (Continued)

22. Truck capacity greater than tank capacity,
operator fails to close tank top flush valve,
inspector fails to verify tank top flush valve position,
operator fails to detect loss of nitrogen through valve,
level alarm HH (LAHH 13) fails to function,
inlet valve (HV 15) fails to close,
level alarm high (LAH 10) fails to low level,
level indication (LI 11) fails to low level.

TABLE 4. FAULT TREE EVENT PROBABILITIES

Component Failure Mode	Base Value	Inspection Interval	Probability/ Frequency
VALUES FOR MONENCO TANK FARM FIRE PROBLEM			
Check valve Fails closed			10^{-4}/D
Control system Fails to close valve	0.29/yr	12 mo.	0.25
Control system Fails to low level	0.29/yr	12 mo.	0.25
Control system Fails to low temperature	0.29/yr	12 mo.	0.25
Flange connection Leak, rupture	$3.x10^{-7}$/hr		$2.6x10^{-3}$/yr
House event Halogenated waste being unloaded	60/yr (one tank)		60/yr
House event Tank being emptied	60/yr (one tank)		60/yr
House event Truck capacity > tank capacity	~ 1		1.0
Interlock logic Fails to prevent valve opening	0.29/yr		0.25
Level alarm high Fails to alarm high level	$2.3x10^{-5}$/hr $2x10^{-5}$/D	12 mo. ~ 60 D/yr	0.18
Level alarm high high Fails to alarm high level	$2.3x10^{-5}$/hr $2x10^{-5}$/D	12 mo. ~ 60 D/yr	0.18

D = Demand(s)

TABLE 4. FAULT TREE EVENT PROBABILITIES (Continued)

Component Failure Mode	Base Value	Inspection Interval	Probability/ Frequency
Level indication Fails to low level	0.41/yr	12 mo.	0.34
Level indication transmitter Fails to low level	1.4×10^{-6}/hr	12 mo.	1.2×10^{-2}
Level switch high high Fails to low level	1.74×10^{-6}/hr	12 mo.	1.5×10^{-2}
Manual valve (flush line) Leak, rupture	10^{-8}/hr		8.8×10^{-5}/yr
Manual valve (sample ports) Leak, rupture	10^{-8}/hr		8.8×10^{-5}/yr
N_2 inlet line Blocked	0.01/yr		10^{-2}
N_2 system No N2 pressure	0.01/yr		10^{-2}
Operator Fails to act, high level	with alarm, indic. without alarm assumes oper. is at controls		~ 0.01 ~ 1.0
Operator Fails to stop pump	with alarm, indic. without alarm assumes oper. is at controls		~ 0.01 ~ 1.0
Operator Fails to close discharge flush valve			~ 0.1
Operator Fails to detect N_2 loss thru valve			~ 1.0
Operator Fails to close top flush valve			~ 0.1

TABLE 4. FAULT TREE EVENT PROBABILITIES (Continued)

Component Failure Mode	Base Value	Inspection Interval	Probability/ Frequency
Operator Fails to close discharge valve after flush			~ 0.1
Operator/Inspector Fails to verify discharge flush valve position			~ 0.1
Operator/Inspector Fails to verify top flush valve position			~ 0.1
Pipeline (general) Leak, rupture	6×10^{-9}/hr		5.3×10^{-5}/yr
Pressure control Fails to high indication	0.47/yr	12 mo.	0.37
Pressure control Fails to low indication	0.47/yr	12 mo.	0.37
Pressure control (assumes air operated) Fails to open	10^{-4}/D	60 D/yr	
Pressure relief valve Fails to open	0.005/yr 10^{-5}/D	12 mo.	5×10^{-3} 10^{-5}/D
Remotely operated valve (assumes motor or solenoid) Fails to close	10^{-3}/D		
Remotely operated valve (assumes motor or solenoid) Fails to open	10^{-3}/D		
Remotely operated valve Transfers closed	9.6×10^{-4}/yr	12 mo.	9.6×10^{-4}
Remotely operated valve Transfers open	9.6×10^{-4}/yr	12 mo.	9.6×10^{-4}

TABLE 4. FAULT TREE EVENT PROBABILITIES (Continued)

Component Failure Mode	Base Value	Inspection Interval	Probability/ Frequency
Remotely operated valve Leak, rupture	10^{-8}/yr		8.8×10^{-5}/yr
Storage tank Leak, rupture			10^{-4}/yr
Temperature alarm high Fails to alarm high temperature	4.6×10^{-5}/hr	12 mo.	0.33
Temperature indication control Fails to low temperature	4.6×10^{-5}/hr	12 mo.	0.33
Temperature indication transmitter Fails to low temperature	10^{-6}/hr	12 mo.	8.7×10^{-3}
Temperature relay Fails to low temperature	10^{-6}/hr	12 mo.	8.7×10^{-3}
Transfer pump (tank filling) Fails to stop	10^{-4}/D	60 D/yr	
Vacuum relief valve Fails to open	0.005/yr 10^{-5}/D	12 mo.	5×10^{-3}
Vent line to overflow tank Blocked	10^{-2}/yr	12 mo.	10^{-2}

ANALYSIS OF THE VAPORIZATION OF METHYLENE CHLORIDE CAUSED BY RADIATION FROM A FIRE OF ORGANIC SLUDGE WASTE IN THE DIKED AREA ADJACENT TO THE HALOGEN-ORGANIC WASTE TANKS

Summary of the Accident Scenario

A leak or a spill of a flammable organic sludge waste in the diked area next to the halogen-organic waste area followed by ignition is assumed. The radiant heat from such a fire may heat and vaporize a halogen-organic waste such as toxic methylene chloride in the adjacent tanks. The vapor is assumed to be vented, at a pressure of 10 psig, through a vent control valve on the halogen-organic waste tanks. The venting to the atmosphere will occur at a height of 10 meters which will protect personnel at the facility but if sufficient methylene chloride is vaporized and vented it may produce an unacceptable concentration at ground level at the facility boundary.

There will probably be substantial fractions of constituents other than methylene chloride in the waste. The constituents and their properties are not available for this analysis, though their influence on the vaporization of the methylene chloride will be postulated.

Description of Storage Tank Area

The portions of the organic waste storage farm of concern are the three halogen-organic waste storage tanks, within a diked area 34 meters by 5.2 meters and the six organic sludge waste tanks within a diked area 34 meters by 15.35 meters. These two sets of tanks are separated by a dike that is 0.4 meters high. The halogen-organic waste tanks are separated from each other by internal dikes 0.4 meters high; the organic sludge tanks are not separated from each other by dikes.

Each of the halogen-organic waste tanks is composed of a cylinder that is 2.1 meters in diameter and 2 meters long atop a cone that is 1.8 meters long. The area of the conical region is 6.93 square meters, the side area of the cylindrical region is 13.19 square meters and the area of the top of the clinder is 3.46 square meters. The volume of each tank is 9.03 cubic meters with a normal load capacity of 8 cubic meters. The top of the

tanks are 5.0 meters above the bottom of the diked area. The centerlines of the halogen waste tanks are 2.6 meters from the dike that separates them from the adjacent organic sludge waste tanks.

Each of the organic sludge waste tanks is similar in shape to the halogen-organic waste tanks but is much larger with a volume of 120 cubic meters. If all of the waste in one completely filled tank of organic sludge waste is spilled or leaked into the diked area around the six tanks it will fill it to a dept of 0.23 meters.

Description of Wastes

Methylene Chloride (CH_2-Cl_2) has a density of 1.13 g/ml, (70.7 lb/cubic foot), a boiling point at atmospheric pressure of 40.1C (104.2F) and at 10 psig of about 53C (127F), a specific heat of 1.206 kJ/kg (0.288 Btu/lb F) and a latent heat of vaporization of 329 kJ/kg (141.5 Btu/lb) at atmospheric pressure and slightly less than that at 10 psig. The other constituents in the methylene chloride waste are not known. Two cases are assumed: (1) the other constituents are similar to methylene chloride in properties other than flammability and (2) the other constituents have a much higher boiling point, but otherwise are the same in properties other than flammability.

The properties of the wastes in the organic sludge tanks are not known. For this analysis it is assumed that they are hydrocarbons that will burn with a sooty flame. It follows from the literature that this will mean a black-body flame with a flame surface temperature of 870C (1600F) which will emit 354,000 kJ/hr per square meter (31,150 Btu per hr. per square ft.). A good assumption is a burning rate of 5 mm/min. which will mean a burning time, for one completely filled tank spilled evenly in the total diked area, of 46 minutes.

Computation of Radiation Flux Factor

It follows from the literature that if the burning waste completely covers the 34 by 15.35 meter diked area the flame will be at least 15 meters high and, of course, 34 meters wide. Since these dimensions

are very large compared to the dimensions of the halogen-organic waste tanks and compared to the distance between those tanks and the dike, the flame, if there is no wind, can be considered to be of infinite height and infinite width to simplify this first order analysis.

To further simplify the analysis the halogen-waste tanks are considered to be simple cylinders with a side area equivalent to the side area of the cylinder plus the area of the cone. This gives a height of 2.9 meters. The bottom of this cylinder is assumed to be even with the top of the dike. An emissivity of 0.8 is assumed as a reasonable value for steel. It is futher assumed that the top and the bottom of the tank will not transmit heat to the wastes inside. The bottom sees only the ground and the top will heat up rapidly because of the vapor space at the top of the tank and then absorb much less heat than the sides which are kept cool by being in contact with the boiling liquid inside. For this same reason reradiation from the sides and bottom is not considered in the analysis.

A simple approximation to the effective area for the middle halogen-organic waste tank being radiated by a one-half infinite flame very close to the tank can obtained by taking one half of the area of the cylindrical surface, 2.9 meters high by 2.1 meters in diameter, and multiplying it by 1/2 for the half-infinite flame and 0.8 for the assumed emissivity of the tank surface. This gives an effective area of:

$$(2.9 \times 2.1 \times \Pi \times 1/2) \times 1/2 \times 0.8 = 3.83 \text{ sq. m. } (41.2 \text{ sq.ft.})$$

A more accurate value could be obtained by integrating vertical elements of the cylinder around the surface of the cylinder and by taking into consideration the varying distance of the cylinder elements from the flame and correcting for the finite height of the cylinder with respect to the half-infinite flame, but this value is adequate for these purposes.

A black body at 870C (1600F) emits 354,000 kJ/hr per square meter (31,150 Btu/hr per square foot); thus the tank will be absorbing 1,354,000 kJ/hr (1,283,500 Btu/hr.). As noted above, reradiation is not included because the temperature of the tank will be kept low by the internal boiling.

Computation of Vaporization of Methylene Chloride

If we assume an ambient temperature in the methylene chloride waste tank of 21C (70F), the energy needed to heat the CH_2Cl_2 to 40.1C (104.2F), the boiling point at atmospheric pressure, is about 22.8 kJ/kg (10 Btu/lb). To heat it to 53C (127F), the approximate boiling point at 10 psig, will take about 38 kJ/kg (17 Btu/lb). The energy needed to vaporize the methylene chloride at atmospheric pessure is 329 kJ/kg (141.5 Btu/lb). At 10 psig the latent heat of vaporization is somewhat less than at atmospheric presssure, though the difference is probably not far from the additional 15 kJ/kg (17 Btu/lb) to heat it to the boiling point at the higher pressure. Therefore the energy to heat and vaporize the methylene chloride is considered to be about 352 kJ/kg (151 Btu/lb).

The density of methylene chloride is 1.134 g/ml. For the moment we will assume that the other waste constituents in the tank have the same density and specific heat as the methylene chloride which is the same as assuming that it is all methylene chloride. Eight cubic meters will weigh about 9,040 kg (19,900 lb). With a heat input to the tank of 1,354,000 kJ/hr (1,283,500 Btu/hr) it will take about 9 minutes to heat the contents of the tank to the boiling point of methylene chloride at atmospheric pressure and 15 minutes at 10 psig.

After the tank has been heated to the boiling point of methylene chloride, about 69 kg (151 lb) of methylene chloride will be vaporized per minute if there is nothing but methylene chloride in the tank or if the boiling points of the other constituents are substantially higher than the boiling point of methylene chloride. That is, during the remaining 37 minutes or 31 minutes, depending upon the pressure, before the fire burns itself out up to 2,550 kg (5,600 lb) of methylene chloride could be vaporized. That is about 28% of the maximum tank load if it were all methylene chloride. If there are other constituents in the tank and their boiling points are about the same as that of methylene chloride a portion of the energy will be used to vaporize the other constituents and the vaporization rate of methylene chloride will be less. If all three halogen-organic

waste tanks are filled with methylene chloride up to 7,650 kg (16,800 lb) could be released by a fire in the organic sludge tank area caused by a leak in one organic sludge tank.

Effect of Insulating the Halogen-organic Tanks

If the halogen-organic tanks were insulated, the time to heat the contents to the vaporization temperature of methylene chloride would be increased and the rate of vaporization thereafter would be decreased. This would provide more time after ignition to implement fire suppression actions.

To be effective, the insulation would have to retain its integrity and insulating properties for an hour or more at surface temperatures substantially above 540C (1,000F). Fiberglass insulation would not survive but there are materials that would.

Preliminary calculations indicate that the time to reach vaporization temperatures can be extended to several hours by insulating the tank with 3 to 4 inches of a high temperature insulating material. The heat transferred to the tank by radiation is less because the surface temperature of an insulated tank will be higher than the surface temperature of a bare tank. The convection losses are higher for the same reason.

ANALYSIS OF THE PROBABILITY OF A FIRE ADJACENT TO THE HALOGEN-ORGANIC TANK AREA THAT COULD CAUSE UNACCEPTABLE VENTING OF METHYLENE CHLORIDE VAPOR TO THE ATMOSPHERE

The sludge tanks in the diked area adjacent to the halogen-organic tank area, are similar enough to the halogen-organic tanks to estimate the likelihood of a leak to be equal to that evaluated for the halogen-organic tanks. That is, a leak can be expected about once in 38 years, per tank. There are factors which may slightly change this estimate:

1. The estimate might be slightly higher (1 to 3%) than that for the halogen-organic tanks due to the additional over-pressure failure mode of the sludge tanks.

2. The operating procedure (frequency of maintenance, etc.) could be somewhat different, impacting the likelihood and type of human error.
3. There may be some hardware differences.

RESULTS AND CONCLUSIONS

The frequency of a leak or spill of halogen-organic waste within the halogen-organic waste tank dikes is estimated to be once in about 38 years per tank.

The probability of a spill that is ignited and heats and vaporizes sufficient waste inside the tank to produce an unacceptable concentration at the boundary of the facility is considerably lower than the probability of a spill, perhaps as much as 20 to 33 times lower, if the ignition frequency of fires at refineries is considered. However, it is difficult to find relevant and thereby convincing data on such things as ignition sources, fire suppression, etc. because they are apt to be site specific.

Before attempting to quantify the other events in the event tree the consequence analysis should be reviewed to determine the probability that a person would be at the boundary of the facility when a once-in-38-year-accident occurred. Also, the probability that the wind direction, velocity and atmospheric stability would be such as to produce the unacceptable concentration at the point on the boundary where the person was located should be determined. All of these items will influence the risk of the fire.

The analysis of the radiation from a fire in the adjacent sludge tank diked area indicates that with uninsulated halogen-organic tanks there may be only 9 to 15 minutes after the fire has fully developed until the tank is heated sufficiently to start vaporizing the methylene chloride. Insulating the tanks will reduce the heating rate and provide time for suppressing the fire, at the expense and inconvenience of the insulation.

The probability of a fire in the dikes adjacent to the halogen-organic waste tanks is about the same as for a fire within the halogen-organic area and subject to the same uncertainties of ignition sources, fire suppression, etc. Again, the probability of other events that contribute to

the consequence should be examined to see if the risk is acceptable before attempting to quantify ignition probability and fire suppression success probability.

Consideration should be given to estimating the cost of high temperature insulation for the halogen-organic waste tanks. At the same time the effectiveness of the insulation should be studied further. The costs will depend upon the temperature and thickness requirements and the thickness will depend upon the duration of the fire since it may only be necessary to delay vaporization of the contents of the tank until the fire burns itself out or is extinguished. Insulation may not provide the same degree of protection to the halogen-organic tanks against a fire within the dike that surrounds the tank and this should be studied further.

APPENDIX A

POSSIBILITY OF PHOSGENE PRODUCTION DURING METHYLENE CHLORIDE/SOLVENT COMBUSTION

Introduction

A technical question has recently arisen as to whether the combustion of methylene chloride was capable of generating phosgene as a product. If so, a secondary question would be at what concentration might the phosgene be produced. For practical reasons arising out of hazardous waste storage considerations, a third and most important question becomes what effect, if any, would the presence of aromatic solvent vapors have on the phosgene-generating-capacity of methylene chloride flames. The following narrative attempts to provide answers to these questions.

It should be stressed at the outset that, to the best of the author's knowledge, definitive answers to these questions are not to be directly found in the technical literature. This is because the experiments designed to provide relevant direct information have not yet been conducted. Hence, the answers here were determined by deductive reasoning and circumstantial evidence.

Analysis

The following are the basic literature[1-9] facts relevant to the problem:

- Thermodynamic, kinetic, and empirical constraints indicate that the final products of complete methylene chloride combustion at stoichiometric and oxygen-rich conditions are carbon dioxide (CO_2) and hydrogen chloride (HCl).[4,5]
- At fuel-rich (air starved) methylene chloride flame conditions, carbon monoxide (CO), chloride (Cl_2), and soot (C_8H) become additional products.[4,5,7]

- Water is not a favored product of methylene chloride combustion.[4,8]
- A major stable intermediate species measured during methylene chloride combustion in methane (CH_4) is trichloroethylene (C_2HCl_3).[5]
- Trichloroethylene has been proven to be the major precursor in the production of measurable quantities of phosgene within flames of chlorinated C_2-hydrocarbons.[1,4,8]
- While up to 20,000 parts per million (ppm) phosgene exists within chlorinated C_2-hydrocarbon flames, only about 25-50 ppm escapes as a final product under non-sooting conditions.[1,2,4,6,8]
- The principal destruction mechanism of the phosgene formed within chlorinated C_2-hydrocarbon flames is decomposition by water, which is very efficient and more favorable under fuel-rich conditions.[2,4]
- More phosgene is emitted from sooting flames of chlorinated C_2-hydrocarbons than from non-sooting ones.[3,6]
- The mechanism for enhanced phosgene production from sooting flames is the heterogeneous recombination reaction between CO and Cl_2 on soot particles.[3,6]
- Of the many chlorinated hydrocarbons, methylene chloride has one of the highest propensities for generating soot.[7]
- The high propensity of methylene chloride for generating soot is comparable to that of benzene or toluene.[7]
- A major intermediate and final product of benzene and toluene combustion is water.[5,7]
- Because the autoignition temperatures of benzene and toluene are lower than that of methylene chloride, the combustion of benzene and toluene in the presence of methylene chloride vapor will commence sooner than that of methylene chloride, placing the combustion products of benzene and toluene (H_2O in particular) within the reaction zone of the methylene chloride flame.[9]

Conclusions

Given these facts, the following are speculative answers to the aforementioned questions:

- Some concentration of phosgene would be expected to be released during the fuel-rich, sooting, nearly water-free conditions that would be indicative of an accidental fire involving neat methylene chloride.
- At present, the probable quantity of phosgene that may be released cannot be ascertained from available information but could be from direct experiments.
- Although not experimentally validated, because of comparable soot yields and finite water yields the presence of benzene or toluene vapors in methylene chloride vapor would be expected to reduce the level of phosgene that neat methylene chloride flames may produce.

In summary, available information indicates that there is reasonable cause to suspect that phosgene may be a product of methylene chloride combustion and that the presence of either benzene or toluene vapors may ameliorate this condition. Moreover, the high capacity of water to destroy phosgene suggests the following fire-fighting approach:

- The application of water fogs to the smoke emitting from accidental fires involving methylene chloride may lessen the danger of toxic phosgene releases via the destruction of the toxic agent.

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